



# Optimisation of Ag loading and alumina characteristics to give sulphur-tolerant Ag/Al<sub>2</sub>O<sub>3</sub> catalyst for H<sub>2</sub>-assisted NH<sub>3</sub>-SCR of NO<sub>x</sub>

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## ABSTRACT

A series of Ag/Al<sub>2</sub>O<sub>3</sub> catalysts with different alumina precursors and different Ag loadings were tested for H<sub>2</sub> assisted NH<sub>3</sub>-SCR of NO. The catalysts were characterised (BET, XRD, NH<sub>3</sub>-TPD, ICP-OES, TEM and UV–vis spectroscopy) and tested as fresh catalyst, during long-term cycling tests with SO<sub>2</sub> present and after the sulphur testing. The aim was to find an optimal configuration of the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst for automotive applications. Catalysts with a high sulphur tolerance during long-term SO<sub>2</sub> cycling (1 h with 10 ppm SO<sub>2</sub> at 250 °C followed by 10 min regeneration at 670 °C, repeated until no difference between cycles was seen) were demonstrated. The high sulphur tolerance and activity was attributed to high surface areas of the catalyst supports, together with a high Ag loading. The high surface area allows a larger NH<sub>3</sub> storage on the surface which is previously reported necessary for the SCR reaction. A higher Ag loading will affect the state of Ag by increasing the ratio of Ag-clusters and particles to highly dispersed Ag ions. SO<sub>2</sub>-poisoned Ag-clusters and particles can be regenerated by the high temperature treatment in the deNO<sub>x</sub> feed, highly dispersed Ag ions cannot.

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## 1. Introduction

Up to now it has been possible to meet the ever stricter emission limits for light-duty diesel vehicles by direct engine management and tuning and use of diesel particulate filters (DPF) and/or oxidation catalysts (DOC). This will not be possible in the future, to meet the upcoming legislation an aftertreatment system will be needed for NO<sub>x</sub> reduction [1]. Options for such reduction are selective catalytic reduction (SCR) by urea, lean NO<sub>x</sub> trap (LNT) and further tuning of the engine like exhaust gas recirculation (EGR). SCR is very effective and is today being widely used for heavy-duty trucks and seems like an attractive way to go, since its high efficiency makes it possible to tune the engines for better fuel efficiency [2]. The first applications with SCR for passenger cars are already on the road in Europe and the USA.

The critical point for all applications is, however, the low-temperature (100–250 °C) activity of the catalyst. In order to reduce NO<sub>x</sub> in the cold part of the test cycles, the engine manufacturers have to take measures to increase the exhaust temperature by engine management, which reduces the overall efficiency of the system. Hydrocarbon (HC)-SCR over Ag/Al<sub>2</sub>O<sub>3</sub> has been known for

quite some time [3] and is widely investigated. Addition of hydrogen is known to enhance the low-temperature activity [4,5]. Richter et al. [6] have showed that Ag/Al<sub>2</sub>O<sub>3</sub> also is active for NH<sub>3</sub>-SCR when H<sub>2</sub> is co-fed; with NO<sub>x</sub> conversion starting at 150 °C. However, since then there have been only few reports about NH<sub>3</sub>-SCR on Ag/Al<sub>2</sub>O<sub>3</sub>.

Although not entirely unambiguous, most studies show that the activity of Ag/Al<sub>2</sub>O<sub>3</sub> is decreased by sulphur which is normally present in automotive exhaust. Those showing the opposite may be attributed to the reaction conditions, reductant, temperature, etc. According to the results of Breen et al. [7], catalyst deactivation by SO<sub>2</sub> only occurs at temperatures of about 230–400 °C for HC-SCR. At lower temperatures, the oxidation of SO<sub>2</sub> to SO<sub>3</sub> supposed to be crucial for the catalyst deactivation does not occur. At higher temperatures, the formed Ag-sulphate becomes unstable. The same results have been showed by Shimizu and Satsuma [8] with deactivation at 250 °C but not at 200 °C for H<sub>2</sub>-assisted NH<sub>3</sub>-SCR. H<sub>2</sub> is reported to facilitate activity regeneration after sulphur poisoning [9]. Different sulphur tolerance for different HC reductants has been shown [10,11]. Testing the sulphur tolerance is therefore very important when evaluating Ag/Al<sub>2</sub>O<sub>3</sub> catalysts for automotive SCR.

This study aims to find the optimal formulation of the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst for H<sub>2</sub>-assisted NH<sub>3</sub>-SCR for automotive applications under realistic conditions. A series of different alumina precursors were thermally pretreated to give alumina supports with varying characteristics to see how the different characteristics influence catalyst performance. Different Ag loadings were also tested. Emphasis of

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this study is on the sulphur tolerance and the regeneration possibilities of the sulphated catalyst.

## 2. Experimental

### 2.1. Catalyst preparation

Four different pseudoboehmite alumina precursors were tested: one from Topsøe, Catapal and Pural from Sasol, and Versal from UOP. The alumina precursors were precalcined at 550, 750 and 1000 °C for 2 h. The resulting alumina samples were then impregnated with AgNO<sub>3</sub> (99.8% purity) by the incipient wetness method to give the desired amount of Ag (1, 2, 3, 4 or 6 wt%). Following the impregnation, the samples were first dried in air at room temperature and then at 100 °C over night. They were thereafter calcined at 550 °C for 2 h. Reference catalysts based on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Puralox SCFa or TH from Sasol) were prepared by the same method. Before testing, the samples were pressed, crushed and sieved to give fractions of 150–300  $\mu$ m.

The catalysts were designated, A, C, P, R and V for Topsøe, Catapal, Pural, reference and Versal alumina, respectively. The letters are followed by the intended Ag loading and by the alumina precalcination temperature, e.g. A1-550 (1 wt% Ag on Topsøe alumina precalcined at 550 °C).

### 2.2. Catalyst characterisation

The specific surface areas ( $S_{\text{BET}}$ ) of the catalysts were measured by N<sub>2</sub>-adsorption by single point or by multipoint BET using either a Quantachrome Monosorb or Autosorb. The difference between results obtained by single and multipoint BET was less than 10% for seven samples tested by both methods;  $S_{\text{BET}}$  is therefore given regardless of method used. Multipoint BET was also used to get information on pore volume and pore size distribution.

The crystal phase of the catalysts was investigated by X-ray diffraction (XRD) on a Philips PW3040/60 diffractometer using Cu K $\alpha$  radiation. The alumina crystal size was estimated applying the Scherrer equation to the reflex from the 440 crystal plane ( $2\theta = 67^\circ$ ).

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) with a Perkin Elmer Optima 3000 was used to verify the Ag-content of the catalysts.

TEM measurements were carried out in a TECNAI T20 transmission electron microscope equipped with an Oxford Instruments EDX detector. For the measurements the catalyst powder was dispersed on a copper TEM grid covered with a lacey carbon film. Images were acquired using DigitalMicrograph from Gatan Inc.

UV–visible reflectance spectroscopy on a Varian Cary 300 was used to investigate the state of Ag in the catalysts. The spectra were converted into the Kubelka–Munk function ( $F(R_\infty)$ ).

Temperature programmed desorption (TPD) of NH<sub>3</sub> was conducted in the catalyst test setup (see below) and with the same amount of catalyst (45 mg). Prior to the experiment, the catalyst was pretreated in a flow of Ar (100 N ml/min) for 30 min at 500 °C. After that the sample was cooled down and NH<sub>3</sub> was then adsorbed at 90 °C (monitored by FTIR), followed by a switch back to Ar-flow to remove gaseous NH<sub>3</sub>. When the NH<sub>3</sub> signal was below 10 ppm, the temperature ramp was started (5 °C/min).

### 2.3. Catalyst activity testing

The catalyst activity was tested in a fixed-bed quartz flow reactor (inner diameter 4 mm). 45 mg of the catalyst was diluted with 100 mg of SiC giving a bed height of ~12 mm. The catalyst was held in place by quartz wool plugs.

A standard deNO<sub>x</sub> feed of 500 ppm NO, 520 ppm NH<sub>3</sub>, 1200 ppm H<sub>2</sub>, 8.3% O<sub>2</sub>, 7% H<sub>2</sub>O and balance Ar was used for activity testing. For

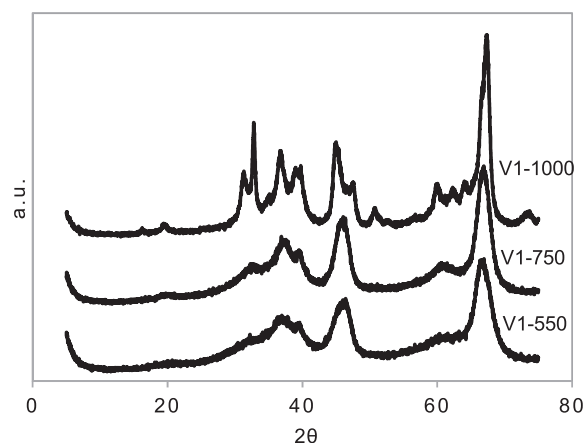


Fig. 1. XRD of Versal, calcined at 550, 750 and 1000 °C, respectively.

sulphur testing, 10 ppm SO<sub>2</sub> was added to the feed. The total flow was 120 N ml/min giving a GHSV of ~50,000 h<sup>-1</sup> based on the whole bed volume (catalyst + SiC) and a GHSV of ~100,000 h<sup>-1</sup> based on the catalyst volume. The gases were controlled by mass flow controllers, and water was fed by a syringe pump (ISCO 100 DM). The gases were either supplied by AGA (Ar and O<sub>2</sub>) or Air Liquide.

During activity testing, the samples were heated to 475 °C and held there for 30 min before being ramped down to 130 °C at a rate of 2 °C/min during which the activity was measured. For sulphur testing, the samples were first heated to 475 °C and held there for 30 min before being ramped down (2.5 °C/min) to 250 °C, where SO<sub>2</sub> was introduced and the activity measurement started. After 1 h at 250 °C, SO<sub>2</sub> was switched off and the temperature was increased to 670 °C and held there for 10 min before being ramped down to 250 °C again. Then the cycle, 1 h at 250 °C followed by 10 min at 670 °C, was repeated until no difference in activity between the sulphation cycles could be seen.

Outlet gases were analysed using a Thermo Fisher Nicolet 6700 FTIR analyzer, equipped with a 2-m gas cell. All gas capillaries and the FTIR gas cell were heated to >130 °C to avoid condensation of water and formation of ammonium nitrate.

NO<sub>x</sub> conversion was calculated as  $(C_{\text{NO}_x,\text{in}} - C_{\text{NO}_x,\text{out}})/C_{\text{NO}_x,\text{in}}$ , where NO<sub>x</sub> was the sum of NO, NO<sub>2</sub> and N<sub>2</sub>O.

## 3. Results

### 3.1. Catalyst characteristics

Characteristics for the different 1 wt% Ag loading catalysts are listed in Table 1. The A- and the V-series had surface areas in the same range for each pretreatment temperature (4–11% variation), the C-series had somewhat lower (11–16%) and the P-series had significantly lower surface areas (48–62%) compared to A. The P-series had a higher pore diameter as compared to the others (3–5 times). The C-series showed a much narrower pore-size distribution than the rest of the samples. The measured Ag loading was close to the target value for the samples tested. The target Ag loading will therefore be used throughout this report.

Increasing the Ag loading did not significantly alter the characteristics as can be seen for P1-1000 and P2-1000. This is in accordance with previously reported results [12,13]. The  $S_{\text{BET}}$  for 1 wt% Ag samples will therefore be used for higher Ag loading samples.

The crystallinity of the samples increased with increased precalcination temperature of the samples seen by XRD spectra. Fig. 1 shows the XRD spectra for the V-series. V1-550 and V1-750 was a mixture of eta and gamma phase and V1-1000 was a mixture of eta

**Table 1**

Characteristics (surface area ( $S_{\text{BET}}$ ), pore volume ( $V_{\text{pore}}$ ), pore diameter ( $D_{\text{pore}}$ ), Ag loading, crystal phase of the alumina, crystal size and  $\text{NO}_x$  conversion at 250 °C before and after testing with sulphur) for the four boehmite alumina-series tested, Topsøe alumina (A), Catapal (C), Pural (P) and Versal (V), together with the reference  $\gamma$ -alumina (R). The alumina designator is followed by the Ag load and by the temperature at which the boehmite was calcined.

Catalyst	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{pore}}$ (cm <sup>3</sup> /g)	$D_{\text{pore}}$ (Å)	Ag loading (wt%)		Alumina phase	Crystal size (Å)	$\text{NO}_x$ conversion at 250 °C	
				Target	Measured			Fresh	After sulphur testing
A1-550	272	–	–	0.99	–	eta/gamma	37	0.56	–
A1-750	214	0.94	171	0.99	–	eta/gamma	43	0.86	–
A1-1000	124	–	–	1.1	0.92	eta/gamma (traces of alpha and theta)	–	0.92	–
C1-550	242	0.49	75	1.0	–	eta/gamma	42	0.77	–
C1-750	179	0.48	101	1.0	1	eta/gamma	51	0.94	0.51
C1-1000	104	–	–	1.0	–	eta/theta	–	0.81	–
P1-550	111	–	–	1.0	–	eta/gamma	85	0.90	–
P1-750	82.2	1.2	514	1.0	0.99	eta/gamma	96	0.72	–
P1-1000	64.4	–	–	1.0	–	theta and delta	–	0.54	0.73
P2-1000	62.2	–	–	2.0	1.8	–	–	0.081	0.56
V1-550	262	–	–	1.0	–	eta/gamma	36	0.64	0.42
V1-750	206	0.92	178	1.0	–	eta/gamma	45	0.83	–
V1-1000	110	–	–	1.0	–	eta/theta	–	0.87	–
R1	142	–	–	1.0	0.87	eta/gamma	57	0.95	–

–, not analysed.

and theta phase. The same trend as for the V-series can be seen for the A-, C- and P-series as well. All the samples calcined at 1000 °C were, at least partly, converted from eta or gamma-alumina to more crystalline phases, alpha, delta and/or theta, Table 1.

The surface areas of the gamma-alumina were proportional to the reciprocal crystal size (Fig. 2). This indicates either a cylindrical or “needle” shape or a spherical shape of the alumina crystals. TEM images of R1 were used to confirm a “needle” shape of the alumina crystals (supporting information, S1).

In conclusion, the aluminas chosen had “needle” shape and displayed a wide range of  $S_{\text{BET}}$ , pore volumes and sizes. We therefore had a representative series of alumina precursors for our tests.

### 3.2. Catalyst activity of 1 wt% Ag samples (without $\text{SO}_2$ )

The catalysts were tested in the standard de $\text{NO}_x$  feed (without  $\text{SO}_2$ ), the temperature was ramped down from 475 to 130 °C at a rate of 2 °C/min. Fig. 3 shows the temperature dependency of  $\text{NO}_x$  conversion for the C-series. C1-750 was almost identical to the reference sample (not shown) and they both showed a very promising activity; comparable to those reported in the literature for Cu- and Fe-zeolites [2]. The  $\text{NH}_3$  conversion followed the  $\text{NO}_x$  conversion close to stoichiometry at temperatures up to 250 °C. The  $\text{N}_2\text{O}$  level was at most 10 ppm and typically below 5 ppm for all the catalysts tested.

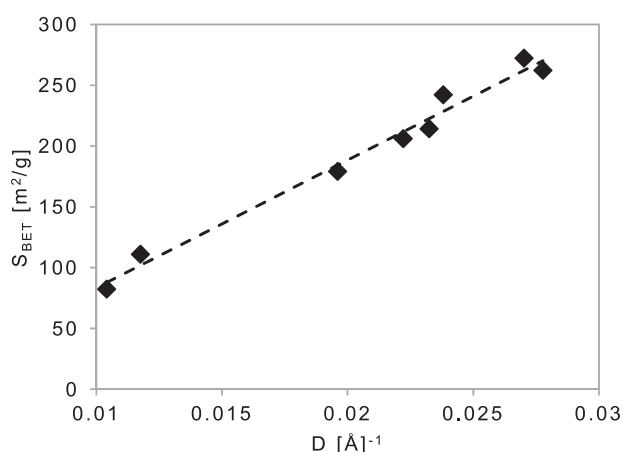


Fig. 2. Correlation between  $S_{\text{BET}}$  and crystal size.

The light-off temperature ( $T_{50}$ ), temperature of 50%  $\text{NO}_x$  conversion, was used to display the low-temperature activity. Fig. 4a shows a clear correlation between  $T_{50}$  and the  $S_{\text{BET}}$  for 1 wt% Ag catalysts. A decrease in  $T_{50}$ , i.e. an increase in low-temperature activity, was seen when the  $S_{\text{BET}}$  was increased from its lowest values. It levelled out at  $S_{\text{BET}} \sim 140 \text{ g/m}^2$ . When  $S_{\text{BET}}$  got higher than  $\sim 200 \text{ g/m}^2$ ,  $T_{50}$  started to increase. Thus, for fresh catalysts there was an optimum  $S_{\text{BET}}$  range of about 140–220  $\text{g/m}^2$ . The same trend with an optimal  $S_{\text{BET}}$ , in the same range, can be seen for  $\text{NO}_x$  conversion at 200 (not shown) and 250 °C (Fig. 4b).

No direct correlation between activity and pore volume or pore size distribution could be seen.

### 3.3. Sulphur tolerance of 1 wt% Ag-samples

Since all diesel fuels normally contain small amounts of sulphur we conducted tests with  $\text{SO}_2$  in the feed. A realistic level of  $\text{SO}_2$  in low-sulphur diesel exhaust is below 1 ppm [7]. Our data for 0.5–10 ppm  $\text{SO}_2$  (not shown) indicate that the degree of sulphur poisoning of Ag/ $\text{Al}_2\text{O}_3$  is cumulative and depends on the total  $\text{SO}_2$  exposure rather than on  $\text{SO}_2$  concentration. Therefore, we used 10 ppm of  $\text{SO}_2$  in the tests to decrease the testing time. Most modern diesel vehicles are equipped with a DPF [2]. The DPF is regenerated

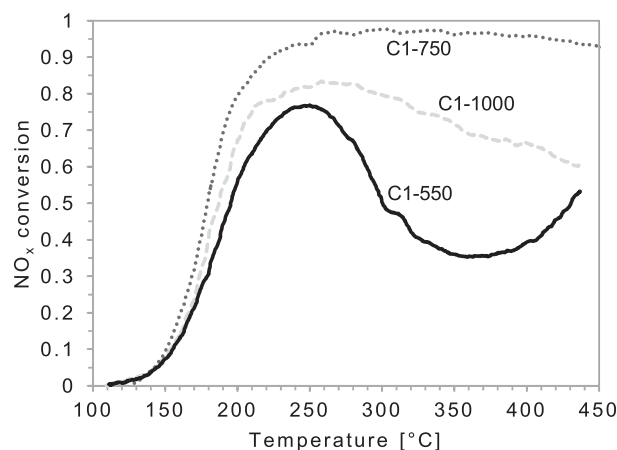
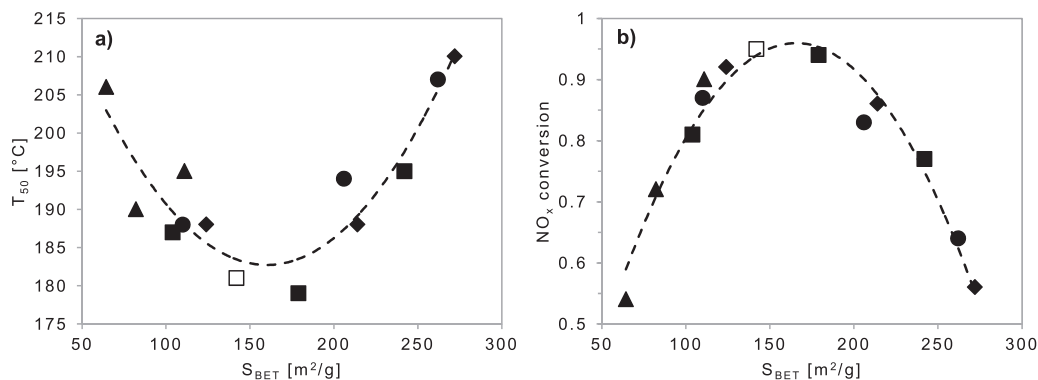
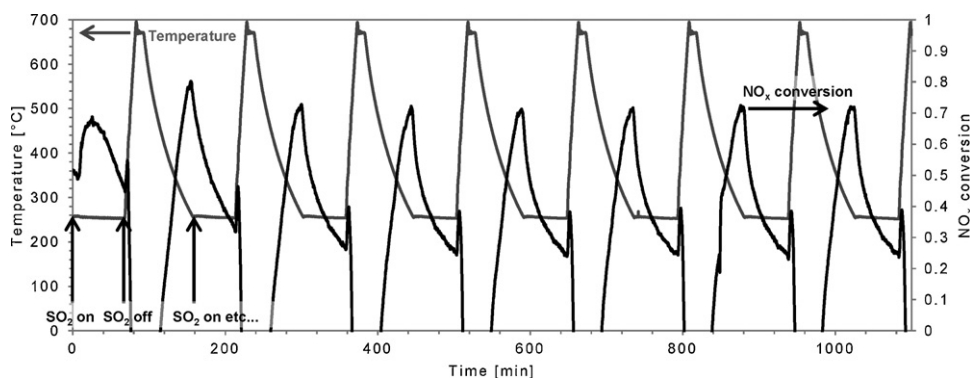


Fig. 3. Dependence of  $\text{NO}_x$  conversion on the reaction temperature for fresh Catapal-series. Reaction conditions: 500 ppm  $\text{NO}$ , 520 ppm  $\text{NH}_3$ , 1200 ppm  $\text{H}_2$ , 8.3%  $\text{O}_2$ , 7%  $\text{H}_2\text{O}$  and balance Ar, GHSV  $\sim 50,000 \text{ h}^{-1}$  (based on bed volume).



**Fig. 4.** (a)  $T_{50}$  (temperature of 50%  $NO_x$  conversion) and (b)  $NO_x$  conversion at 250 °C; for fresh sample-series of A (“diamond”), C (“filled square”), P (“triangle”), V (“circle”) and R (“open square”) 1 wt% Ag catalysts with respect to  $S_{BET}$ . Reaction conditions: 500 ppm NO, 520 ppm  $NH_3$ , 1200 ppm  $H_2$ , 8.3%  $O_2$ , 7%  $H_2O$  and balance Ar, GHSV  $\sim 50,000 h^{-1}$  (based on bed volume).



**Fig. 5.** Sulphur tolerance – regeneration cycling for P1-1000. Only the first eight cycles are shown. Reaction conditions: 500 ppm NO, 520 ppm  $NH_3$ , 1200 ppm  $H_2$ , 0 or 10 ppm  $SO_2$ , 8.3%  $O_2$ , 7%  $H_2O$  and balance  $N_2$ , GHSV  $\sim 50,000 h^{-1}$  (based on bed volume).

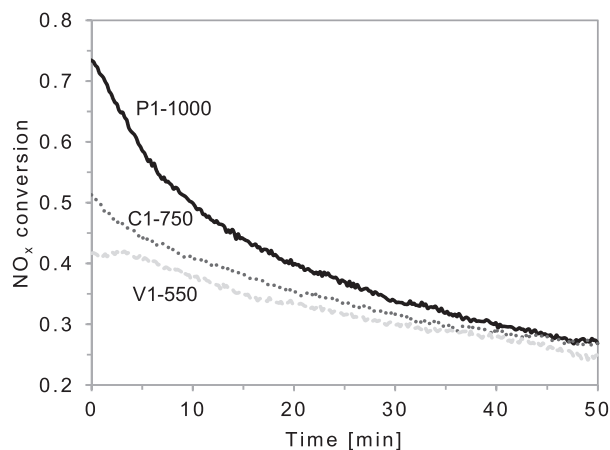
by burning off the soot at elevated temperatures at regular intervals. To mimic real life conditions and to investigate whether the catalyst could be regenerated by an increased temperature or not, like during DPF regeneration, the catalysts were first subjected to sulphur for 1 h at 250 °C. This roughly corresponds to the amount of sulphur a typical catalyst is subjected to between DPF regenerations, about 900 km of driving [14]. Sulphur was then turned off, and the temperature was increased to 670 °C and held there for 10 min to simulate regeneration of the catalyst. When the temperature once again had reached 250 °C, sulphur was again turned on and the cycle started all over again (Fig. 5). This was repeated 20 times giving a total time on stream with sulphur of 20 h.

The sulphur tolerance was tested for three of the samples representing low, medium and high surface areas to see if the same trend as for fresh catalysts with an optimal  $S_{BET}$  around 140–220 g/m<sup>2</sup> could be seen. The samples tested were P1-1000, C1-750 and V1-550. Fig. 5 shows the first eight cycles for P1-1000; the trends for C1-750 and V1-500 (not shown) were similar. All catalysts were severely deactivated by  $SO_2$  and it was possible to regenerate part of the activity. Both P1-1000 and V1-550 showed a higher SCR activity at the start of cycle two (regenerated activity) compared to at the start of cycle one (fresh activity). The regenerated activity declined after cycle two before it reached a steady value. C1-750, on the other hand, did not show this increase in activity between the start of cycle one and cycle two.

After 3–6 cycles, the regenerated (after 10 min at 670 °C without  $SO_2$ ) and sulphated activity (after 1 h with  $SO_2$ ) became stabilised and the deactivation profile was identical for subsequent cycles, this will be referred to as “steady-state”. Fig. 6 shows one sulphation cycle at this steady-state for the three catalysts tested. The low surface-area sample (P1-1000) showed the highest

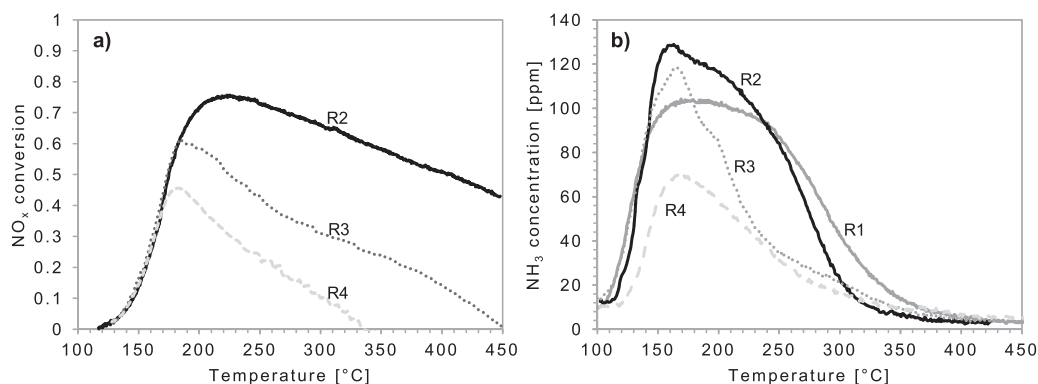
regenerated activity followed by the medium and high surface area samples (C1-750 and V1-550). P1-1000 showed a much more rapid decrease in  $NO_x$  conversion. At the end of the sulphation cycle all samples had the same activity.

An interesting and surprising observation was that P1-1000 had a higher  $NO_x$  conversion after exposure to  $SO_2$  and regeneration (at steady-state) than it had as a fresh sample under the same



**Fig. 6.**  $NO_x$  conversion for one sulphur tolerance test cycle at steady-state (no change in deactivation profile between cycles) for P1-1000, C1-750 and V1-550, representing low (64 m<sup>2</sup>/g), medium (180 m<sup>2</sup>/g) and high (260 m<sup>2</sup>/g) surface areas, respectively. Reaction conditions:  $T=250$  °C, 500 ppm NO, 520 ppm  $NH_3$ , 1200 ppm  $H_2$ , 10 ppm  $SO_2$ , 8.3%  $O_2$ , 7%  $H_2O$  and balance Ar, GHSV  $\sim 50,000 h^{-1}$  (based on bed volume).





**Fig. 7.** (a) Dependence of NO<sub>x</sub> conversion on the reaction temperature for fresh reference-series, 2–4 wt% Ag (R2, R3 and R4). Reaction conditions: 500 ppm NO, 520 ppm NH<sub>3</sub>, 1200 ppm H<sub>2</sub>, 8.3% O<sub>2</sub>, 7% H<sub>2</sub>O and balance Ar, GHSV ~50,000 h<sup>-1</sup> (based on bed volume) and (b) NH<sub>3</sub>-TPD profiles for reference-series with 1–4 wt% Ag (R1, R2, R3 and R4). Conditions: 100 N ml/min Ar, 5 °C/min ramp.

conditions; 72 and 54%, respectively (Figs. 4b and 6). The catalyst was activated by sulphur. The activity was also increased for about 30 min during cycle one, before decreasing (Fig. 5). An initial increase of activity upon sulphur poisoning was also reported for propane and propene-SCR by Shimizu et al. [9] and Park and Boyer [12], the latter attributed it to the formation of silver-sulphate.

The higher regenerated NO<sub>x</sub> conversion of P1-1000 indicates that a high Ag loading/*S*<sub>BET</sub> is advantageous for higher sulphur tolerance for the catalyst. Higher Ag loading samples were therefore prepared.

### 3.4. Catalytic activity of higher Ag loading catalysts

Fig. 7a compares the NO<sub>x</sub> conversion for fresh R-catalyst with 2, 3 and 4 wt% Ag in the standard deNO<sub>x</sub> feed during temperature ramping (475–130 °C). The activity curves follow each other closely up to ~170 °C for the three samples. The NO<sub>x</sub> conversion for the higher Ag loading catalysts was significantly lower at higher temperatures. This cannot entirely be explained by unselective NH<sub>3</sub> oxidation since NH<sub>3</sub> conversion followed the NO<sub>x</sub> conversion up to 250 °C for the 3 and 4 wt% Ag-samples (through the whole temperature range for the 2 wt% Ag sample). At temperatures above 250 °C, NH<sub>3</sub> oxidation could contribute to the decrease in NO<sub>x</sub> conversion. A lack of NH<sub>3</sub> adsorbed on the catalyst surface, which is thought to be necessary for the NH<sub>3</sub>-SCR of NO<sub>x</sub> [15,16], can be a possible explanation for low NO<sub>x</sub> conversion for high Ag loading catalysts. NH<sub>3</sub> adsorption capacity was estimated by NH<sub>3</sub>-TPD for R1, R2, R3 and R4 (Fig. 7b). The ammonia adsorption capacity at temperatures above 200 °C decreased when the Ag loading increased above 2 wt%. It can be seen as a general trend that a higher amount of Ag led to lower activity at higher temperatures due to lower NH<sub>3</sub> adsorption capacity, possibly due to Ag blocking the strongest NH<sub>3</sub> adsorption acid sites on the alumina.

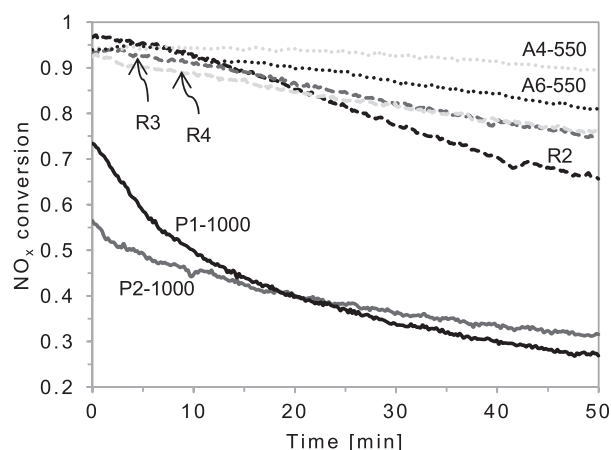
### 3.5. Sulphur tolerance of higher Ag loading catalysts

P2-1000, R2, R3, R4, A4-550 and A6-550 catalysts were prepared and tested for sulphur tolerance in the same way as previously done with 1 wt% Ag catalysts (10 ppm SO<sub>2</sub> for 1 h at 250 °C followed by 10 min regeneration at 670 °C). This was repeated until no difference could be seen between the cycles (steady-state), at least ten cycles (10 h on stream with SO<sub>2</sub>) were run.

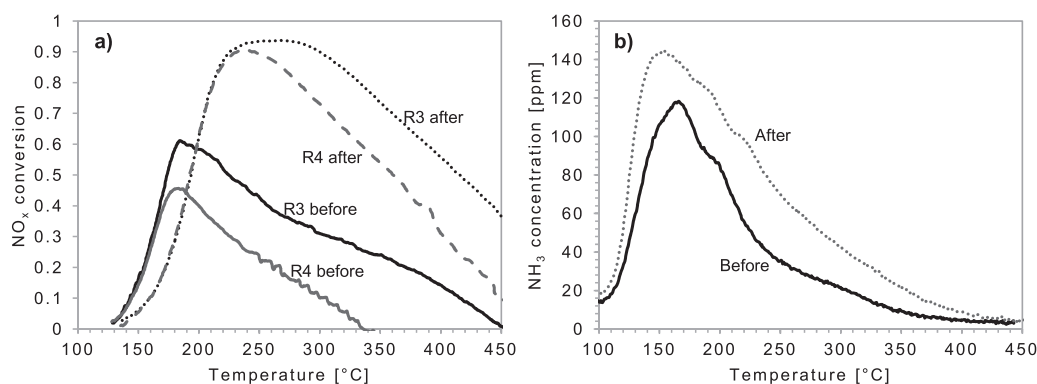
All tested catalysts showed a similar behaviour as that of P1-1000 (Fig. 5) with an initial increase of the activity during cycle one and an increased activity after regeneration at the beginning of cycle two. The regenerated and sulphated activities became stable after a few cycles and no differences could be seen between

subsequent cycles, steady-state. Fig. 8 shows the deactivation during one of these steady-state sulphation-cycles; P1-1000 was included for comparison. Increasing the Ag loading did not increase the regenerated activity for the low *S*<sub>BET</sub>-sample (P1- and P2-1000). P2-1000 did, on the other hand, show a slower deactivation than P1-1000 when SO<sub>2</sub> was present in the feed. The higher *S*<sub>BET</sub>-samples all showed a similar regenerated activity around 93–94% NO<sub>x</sub> conversion. R2 showed a slightly higher regenerated activity but at the same time a more rapid deactivation; i.e. lower sulphur tolerance. A4-550 was the most sulphur-tolerant catalyst and showed a very low deactivation during the test. NO<sub>x</sub> conversion dropped from 94 to 88%, corresponding to a decrease in NO<sub>x</sub> reduction rate of 25% (assuming first order kinetics and the reactor being an ideal plug-flow-reactor). R3, and R4 showed an almost identical deactivation profile; this together with the fact that A6-550 showed lower sulphur tolerance than A4-550 points to that there is an optimum Ag load for each alumina type (likely linked to different *S*<sub>BET</sub> giving different amounts of acid sites).

Fig. 9a shows a comparison of the activity during temperature ramp-down in standard deNO<sub>x</sub> feed (no SO<sub>2</sub>) for R3 and R4 before and after sulphur testing. R3 and R4 showed very similar behaviour up to ~170 °C for fresh and up to ~240 °C for sulphated catalysts. At higher temperatures the NO<sub>x</sub> conversion profiles deviated a lot. This stresses the necessity to combine different testing, in this case



**Fig. 8.** NO<sub>x</sub> conversion for one sulphur tolerance test cycle at steady-state (no change in deactivation profile between cycles) for higher Ag load samples, P1-1000, P2-1000, R2, R3, R4, A4-550 and A6-550, representing low (64 m<sup>2</sup>/g), medium (140 m<sup>2</sup>/g) and high (270 m<sup>2</sup>/g) surface areas, respectively. Reaction conditions: T=250 °C, 500 ppm NO, 520 ppm NH<sub>3</sub>, 1200 ppm H<sub>2</sub>, 10 ppm SO<sub>2</sub>, 8.3% O<sub>2</sub>, 7% H<sub>2</sub>O and balance Ar, GHSV ~50,000 h<sup>-1</sup> (based on bed volume).

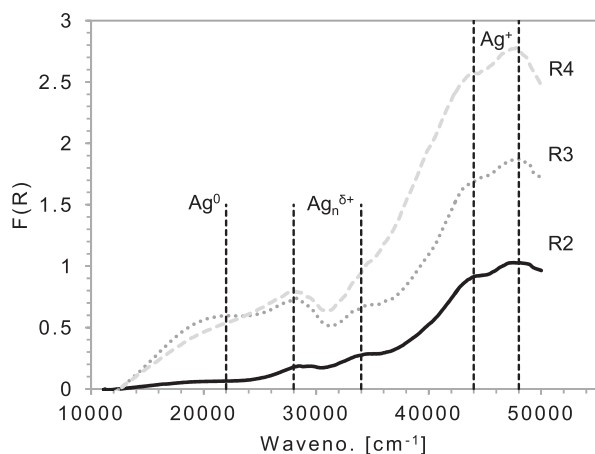


**Fig. 9.** (a) Comparison of the dependence of NO<sub>x</sub> conversion on the reaction temperature for reference catalyst, 3 and 4 wt% Ag (R3 and R4), before and after testing with sulphur. Reaction conditions: 500 ppm NO, 520 ppm NH<sub>3</sub>, 1200 ppm H<sub>2</sub>, 8.3% O<sub>2</sub>, 7% H<sub>2</sub>O and balance Ar, GHSV ~50,000 h<sup>-1</sup> (based on bed volume) and (b) NH<sub>3</sub>-TPD profiles for reference catalyst with 3 wt% Ag (R3) before and after testing with sulphur. Conditions: 100 Nl/min Ar, 5 °C/min ramp.

sulphur testing at 250 °C and temperature ramping (475–130 °C), to be able to distinguish the performance of different catalysts. By subjecting the catalyst to SO<sub>2</sub> followed by regeneration there is a huge gain in maximum and higher-temperature activity. At the same time, the low-temperature activity cannot be fully regained. Fig. 9b shows the difference in NH<sub>3</sub> adsorption capacity before and after testing with sulphur for 3 wt% Ag reference catalyst. Sulphur increased the NH<sub>3</sub> adsorption capacity which could be part of the explanation for the increase in activity after testing with sulphur.

### 3.6. UV–vis spectra

Many reports show that increasing the Ag loading will affect the state of Ag [17–21]. An increase in Ag loading will give more Ag clusters/nanoparticles relative to highly dispersed Ag-ions. UV–vis spectroscopy is a widely used method to investigate the state of Ag [17–21]. Spectra were taken for P1- and P2-1000, A4- and A6-550 and R2, R3 and R4. Fig. 10 shows the spectra for the latter series. Broad peaks were seen at bands of around 21,000–23,000, 28,000, 34,000–35,000 and above 40,000 cm<sup>-1</sup>. The band at 22,000 cm<sup>-1</sup> has been attributed to larger metallic Ag nanoparticles (~10 nm), the peaks at 28,000 and 34,000–35,000 cm<sup>-1</sup> to Ag<sub>n</sub><sup>δ+</sup>-clusters and above 40,000 cm<sup>-1</sup> to dispersed Ag<sup>+</sup>-ions [22,23]. From Fig. 10 it is clear that the intensities for the bands attributed to Ag-clusters and nanoparticles increased as the Ag loading increased from 2 to 3 and 4 wt%. The same trend with an increase in the amounts of Ag present as clusters or nanoparticles in the catalysts with higher Ag loading was also seen for the A- and P-series (not shown). Thus, the UV–vis



**Fig. 10.** UV–vis spectra for reference-series with 2–4 wt% Ag. The major peaks attributed to Ag<sup>0</sup>, Ag<sub>n</sub><sup>δ+</sup> and Ag<sup>+</sup> are indicated.

results qualitatively indicate that the samples with higher Ag loading had a higher ratio of cluster and particles to dispersed ions. These indications are in agreement with those previously reported in the literature.

## 4. Discussion

The correlation between  $T_{50}$  and NO<sub>x</sub> conversion at 250 °C (near maximum) and  $S_{BET}$  (Fig. 4) is clear. It should be emphasised that the different  $S_{BET}$  stems from different calcinations temperatures of the alumina precursor and that other characteristics like crystal phase also is affected (Fig. 1). Different crystal phases of the alumina may affect the Ag and alumina interaction. Zhang and Kaliaguine [13] concluded that impregnation of AlOOH with Ag gave a Ag–O–Al bond whereas impregnation of Ag on a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> gave more dispersed Ag due to less –OH groups available. In our study all precursors were precalcined and the alumina were dehydrated meaning the effect of surface –OH groups would be small. It was only the samples calcined at 1000 °C that showed any significant change in crystal phase of the alumina. The results for those samples did not stand out from the others. We, therefore, attribute the difference in deNO<sub>x</sub> activity for the different catalysts to differences in surface area between the precursors rather than an effect of difference in crystal phase and crystallinity. However,  $S_{BET}$  and crystallinity (Fig. 2) are closely related to each other so influence on the performance from different crystallinity of the samples cannot be ruled out. We also found no correlation between other textural characteristics, such as pore volume or pore size distribution and activity. This supports the hypothesis that it is the correlation between Ag loading and surface area of the alumina catalysts carrier that is the influencing parameter. A higher Ag loading/ $S_{BET}$  will affect the dispersion and state of Ag as well as the acid–basic properties of the alumina support. Different Ag loadings will therefore correspond to different optimal  $S_{BET}$  and vice versa, this was also concluded by Zhang and Kaliaguine [13] for HC-SCR reaction.

Fig. 6 shows the importance of Ag loading/ $S_{BET}$  for sulphur tolerance, the low  $S_{BET}$  sample (P1-1000) shows the highest regenerated activity. However, there was a limit to the maximum possible activity for low  $S_{BET}$  catalysts, shown by a lower regenerated activity for P2-1000 (Fig. 8). We attribute this to a lack of available NH<sub>3</sub> on the surface due to fewer acid sites available for NH<sub>3</sub> adsorption. The latter was demonstrated by TPD (Fig. 7b) for reference catalyst catalysts with different Ag loading (1–4 wt%). Alumina carriers with higher  $S_{BET}$  are therefore of more interest for production of catalysts with higher activity. The higher number of acid sites stems from the higher geometrical area and the amounts of acid sites are proportional to the  $S_{BET}$ . To obtain similar or higher Ag loading/ $S_{BET}$

as for the most sulphur-tolerant 1 wt% sample (P1-1000), more Ag was loaded on to the high  $S_{\text{BET}}$  alumina. The samples (R2, R3, R4, A4- and A6-550) all demonstrated much higher regenerated  $\text{NO}_x$  conversion (93–97%) compared to any of the 1 wt% Ag/ $\text{Al}_2\text{O}_3$ . R4 showed a sulphur tolerance very similar to the one for R3, and A6-500 showed a lower tolerance than A4-550 indicating that there is an optimal Ag loading for sulphur tolerance; the same trend that could be seen for fresh catalysts. Ag loading/ $S_{\text{BET}}$  is a trade-off between having as many stabilised active Ag-sites as possible and having acid sites available for  $\text{NH}_3$  adsorption.

We attribute the large difference in sulphur tolerance between low and high Ag loading catalysts to the different types of Ag present, highly dispersed Ag-ions and partly charged Ag-clusters and metallic Ag-nanoparticles. Similar conclusions were made by Shimizu et al. [9], who investigated sulphur tolerance for propane-SCR over Ag/ $\text{Al}_2\text{O}_3$  with different Ag loadings. They concluded that  $\text{H}_2$  promotes removal of Ag-sulphates and that higher Ag loading samples gave higher sulphur tolerance. The samples with the highest Ag loading had a larger part of the Ag present as partly charged Ag-clusters compared to lower loading samples. For HC-SCR dispersed Ag is believed to be most active for NO SCR with a high selectivity towards  $\text{N}_2$ . Ag-clusters and particles are, on the other hand, more active for HC combustion and NO reduction to unwanted  $\text{N}_2\text{O}$  [18]. We observed that the  $\text{NH}_3$  conversion deviated from that of NO at temperatures above 250–300 °C and a somewhat higher  $\text{N}_2\text{O}$  production over fresh catalysts with higher Ag loading in agreement with findings for HC-SCR. After sulphation and regeneration, however, no unwanted  $\text{NH}_3$  oxidation and  $\text{N}_2\text{O}$  levels below 3–5 ppm were seen. Any  $\text{NH}_3$  oxidation is unwanted, since it means that less  $\text{NH}_3$  is available as reductant. Moreover, oxidation of  $\text{NH}_3$  to NO or  $\text{N}_2\text{O}$  lead to negative  $\text{NO}_x$  conversion.

When the catalyst is subjected to  $\text{SO}_2$  both the Ag and the alumina support will be affected [24]. The difference is that Ag-sulphates can be decomposed at the regeneration temperature used in this report (670 °C) whereas alumina sulphates cannot [25,26]. We suggest in a previous study [14] that it is only the Ag-clusters and particles, and not the dispersed Ag-ions that can be regenerated. After a few sulphation cycles all alumina is permanently sulphated, leading to blockage of the dispersed Ag-ions. This would then explain why the activity in the lowest temperature range, where Ag-ions are believed active, are permanently lost (Fig. 9a). The Ag-clusters and particles are, on the other hand regenerated. When  $\text{SO}_2$  once again is switched on, the activity starts to decrease as Ag-sulphates are formed. Meunier and Ross [24] reported that sulphation of alumina only to a small extent affects the catalyst activity at high temperatures (486 °C) for HC-SCR and that it is the sulphation of Ag that is responsible for the decrease in activity reported. They also suggested that the reaction takes place in a different way over dispersed Ag-ions and over metallic (clusters and particles) Ag which could also be part of the explanation of the higher activity of the catalysts with more Ag-clusters and particles seen after exposure to  $\text{SO}_2$ . The fact that the sulphation of alumina only plays a minor roll in the total decrease in activity at higher temperatures (above 200 °C) is supported by the results in this report with high  $\text{NO}_x$  conversion over sulphated catalysts (Fig. 9a). However, the sulphation of alumina will severely affect the catalytic activity at lower temperatures, possibly by blocking active dispersed Ag-ions.

One reason for the increase in high-temperature activity seen for sulphated catalysts (Fig. 9a) is that sulphation of the alumina leads to formation of strong Lewis acid sites on the catalyst surface [27] and, thus, a higher  $\text{NH}_3$ -adsorption capacity at higher temperatures which was also shown by  $\text{NH}_3$ -TPD (Fig. 9b). The increase in  $\text{NH}_3$  adsorption capacity is believed to explain the initial increase in activity during the first 30 min of the first sulphation cycle. It is also believed to partly explain the increase in

regenerated activity between the first and the second sulphation cycle for the high Ag loading/ $S_{\text{BET}}$  samples, e.g. P1-1000 (Fig. 5). The fresh catalyst was limited by the availability of adsorbed ammonia. When the catalyst was subjected to sulphur, the ammonia adsorption capacity and thus the activity increased, seen as the initial (30 min) activity increase. Reduction of Ag-ions to Ag-clusters could also contribute [9]. Yoon et al. [21] showed that the amount of Ag-clusters/nanoparticles increases as the calcination temperature was increased for their 2 wt% Ag-catalyst (550–800 °C). The high regeneration temperature of 670 °C we used will therefore likely lead to the formation of more Ag-clusters on the catalyst surface as well as other structural changes. These changes are stabilised after a few sulphation and regeneration cycles and are believed, beside the increased  $\text{NH}_3$  adsorption capacity, to be another reason for to the enhanced activity of the sulphated samples. Sulphation also seems to block  $\text{NH}_3$  oxidation sites, since  $\text{NO}_x$  and  $\text{NH}_3$  conversion profiles were close to stoichiometric during the whole temperature range tested for sulphated catalysts. The suppression of  $\text{NH}_3$  oxidation is, however, only of importance at temperatures above 250–300 °C where fresh high Ag loading catalysts started to show unselective  $\text{NH}_3$  oxidation. Similar conclusions were made by Demidyuk et al. for HC-SCR [28].

Our results indicate that having a larger part of Ag present as Ag-clusters is favourable over having larger Ag-nanoparticles. The oxidation of  $\text{NH}_3$  increased for all the fresh catalyst series as the  $S_{\text{BET}}$  was decreased; the samples with the highest Ag to  $S_{\text{BET}}$  ratio probably had the highest amounts of Ag nanoparticles. The  $\text{NH}_3$  oxidation was also most prominent over P2-1000 and R4; the samples with the highest Ag loading/ $S_{\text{BET}}$ . Large Ag-particles have been reported to be more active for  $\text{NH}_3$  oxidation [29,30]. A4-550, showing the best performance, had a medium Ag to  $S_{\text{BET}}$  ratio indicating less Ag-nanoparticles. It still had, as indicated by the UV-vis spectra, a favourably higher ratio of clusters and particles to highly dispersed Ag-ions when compared to the lowest Ag loading samples. This indicates that Ag-clusters are more active for  $\text{NO}_x$  SCR than metallic Ag-particles. Formation of larger Ag-particles will also reduce the relative amount of available Ag-sites which also is likely to give a lower activity.

## 5. Conclusions

A series of Ag/ $\text{Al}_2\text{O}_3$  catalysts with different alumina precursors and different Ag loadings giving a wide range of characteristics was prepared. Most of the samples tested were gamma alumina; those precalcined at 1000 °C were of higher alumina phases. Alumina phase changes are not believed to affect the performance to any larger extent. The catalysts were tested as fresh catalysts, during and after sulphation. Catalysts with high sulphur tolerance were demonstrated ( $\text{NO}_x$  conversion ~90% at 250 °C with 10 ppm  $\text{SO}_2$ ). At  $T > 200$  °C catalysts with high Ag loading were activated after short sulphur exposure. Low-temperature activity (<200 °C) was, however, lost after exposure to sulphur with a shift of  $T_{50}$  by 15–20 °C towards higher temperatures for the best catalysts. The completely different results obtained for fresh and sulphated catalysts stresses the importance to include sulphur in the activity testing; or at least as a type of “de-greening” process.

To obtain high activity and sulphur tolerance we found that the important characteristic of the support is a high  $S_{\text{BET}}$  which is proportional to the amount of acid sites. This together with a high Ag loading gives a sulphur tolerant and active catalyst. Having as many stabilised active Ag-sites as possible (a high Ag loading) and having acid sites available for  $\text{NH}_3$  adsorption ( $S_{\text{BET}}$ ) is a trade-off. A high  $S_{\text{BET}}$  is needed because it gives a higher overall  $\text{NH}_3$  adsorption capacity (more acid sites) compared to low  $S_{\text{BET}}$  catalysts. A high Ag loading/ $S_{\text{BET}}$  is wanted since it affects the state of Ag by

increasing the ratio of Ag-clusters and particles to highly dispersed Ag ions. SO<sub>2</sub>-poisoned Ag-clusters and particles can be regenerated by treatment in the deNO<sub>x</sub> feed at 670 °C, highly dispersed Ag ions cannot. In practise this regeneration should coincide with the DPF regeneration in an engine exhaust.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2012.06.014>.

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